

REMARKS

Further and favorable reconsideration is respectfully requested in view of the foregoing amendments and the following remarks.

Thus, each of claims 1 and 12, which are the only independent claims in the application, has been amended to require that the copolymer of vinylidene fluoride monomer and hydrophilic monomer is "obtained by copolymerization". Support for this expression is apparent from the specification in general, and more particularly, for example, page 3, line 25 and page 4, lines 16 and 20.

The patentability of the presently claimed invention over the disclosures of the references relied upon by the Examiner in rejecting the claims will be apparent upon consideration of the following remarks.

Thus, the rejection of claims 1, 4-7 and 10-11 under 35 U.S.C. 102(b) as being anticipated by Muller et al. (US '401), as well as the rejection of claims 1 and 3-4 under 35 U.S.C. 102(b) as being anticipated by Joffe et al. (US '163), the rejection of claims 8-9 under 35 U.S.C. 102(b) or 35 U.S.C. 103(a) as being anticipated or suggested by Muller et al., and the rejection of claims 8-9 under 35 U.S.C. 102(b) or 35 U.S.C. 103(a) as being anticipated or suggested by Joffe et al., are respectfully traversed.

As indicated above, both claims 1 and 12 have been amended to clarify that the porous membrane of the present invention comprises a (hydrophilic) copolymer **obtained by copolymerization** of vinylidene fluoride monomer and a small amount of a hydrophilic monomer. Such a hydrophilic copolymer formed by monomer-to-monomer reaction (copolymerization) is provided with persistent and durable hydrophilicity due to a **firm bonding** between polymerized units of vinylidene fluoride monomer and polymerized units of hydrophilic monomer. Thus, although the expression "obtained by copolymerization" introduced into the claims is a product-by-process limitation, it reflects the structure of the copolymer in the relative degree of bonding between the vinylidene fluoride monomer and hydrophilic monomer, as compared to the polymers in the references, which as noted by the Examiner, are obtained by **graft-polymerization**.

Thus, Muller et al. disclose hydrophilic monomers at column 1, line 61, which are graft-polymerized onto PVDF membrane (column 1, lines 54-55). A graft polymer formed by polymer-to-monomer reaction, although sometimes classified as a type of copolymer, is clearly different from a copolymer as used in the present invention obtained by monomer-to-monomer reaction (copolymerization). This is clear from the classification disclosed in Table 1.2 at page I/2 of Polymer Handbook, Fourth Edition, where “graft” is referred to as “(side blocks chains connected to main chain)”, and page 29, lines 17-15 from the bottom of Polymer Chemistry, 1973 which describes: “Polymers with structures similar to those shown in Figure 28/1 are called graft copolymers if the side chains have a different structural unit from the main chain”. Copies of these reference materials are enclosed.

Moreover, such graft-polymerization of a hydrophilic monomer onto a PVDF membrane is accompanied with several difficulties, such as blockage of the pores by the polymerized hydrophilic polymer, as discussed at column 1, line 63 - column 2, line 2 of Muller et al. These difficulties are similar to those of (1) to (3) discussed at page 2, lines 18-25 of the present specification regarding a polyvinylpyrrolidone crosslinked product on a wet PVDF membrane (JP-A 11-302438).

The invention of Muller et al. aims at providing a solution to the difficulties of the above-discussed prior art by using a homogeneous mixture of PVDF and hydrophilic polymer as a matrix of the porous or capillary membrane.

Thus, polyvinyl acetate disclosed at column 2, line 22 of Muller et al. is used in a mixture with PVDF forming a membrane (column 2, lines 5-6). No chemical connection is formed with the matrix PVDF. On the other hand, hydrophilic monomers disclosed at column 2, lines 58-59 are optionally copolymerized with methyl acrylate and ethyl acrylate to provide a second (co)polymer to be homogeneously mixed with PVDF. Again, no chemical connection is formed between the (co)polymer and PVDF.

Example 24 of Muller et al. merely discloses a mixture of 90.5 wt% of PVDF and 9.5 wt% of PMA (i.e., polymethyl acrylate).

Consequently, no copolymer formed by monomer-to-monomer reaction (copolymerization) of vinylidene fluoride monomer and hydrophilic monomer, as used in the

present invention, is disclosed or suggested as a material for a porous membrane in Muller et al.

Joffee et al. also fail to disclose a copolymer formed by monomer-to-monomer reaction (copolymerization) of vinylidene fluoride monomer and hydrophilic monomer, used as a matrix of a porous membrane in the present invention.

As mentioned by the Examiner, Joffee et al. (column 4, line 66 - column 5, line 57; columns 9-10, Examples 1-5; column 10, Table 1) disclose the grafting of hydrophilic monomers onto a PVDF membrane. The resultant polymer is however a graft copolymer (polymer-to-monomer reaction product) which has a clearly different chemical structure from the copolymer formed by monomer-to-monomer reaction (copolymerization) of vinylidene fluoride monomer and hydrophilic monomer for providing a matrix of the porous membrane in the present invention, as discussed above in detail with reference to the Muller et al. reference.

For these reasons, Applicants take the position that the presently claimed invention is neither anticipated nor suggested by either of the Muller et al. and Joffee et al. references.

The rejection of claims 2-6 under 35 U.S.C. 103(a) as being unpatentable over Muller et al. in view of Steuck (US '533), as well as the rejection of claim 12 under 35 U.S.C. 103(a) as being unpatentable over Muller et al. in view of Takamura et al. (US '773), are respectfully traversed.

The comments set forth above concerning the Muller et al. reference are equally applicable to both of these rejections.

The Examiner applies the secondary references for features that are set forth in dependent claims of the present application. Therefore, in view of the distinctions between the independent claims of the present application and the Muller et al. reference as discussed above, it is apparent that even if the secondary references were combined with Muller et al., the result of such combination would still not suggest the invention as set forth in claims 2-6 or 12.

Therefore, in view of the foregoing amendments and remarks, it is submitted that each of the grounds of rejection set forth by the Examiner has been overcome, and that the application is in condition for allowance. Such allowance is solicited.

Respectfully submitted,

Takumi KATSURAO et al.

For: Michael R. Davis

Michael R. Davis

Registration No. 25,134

Attorney for Applicants

By: Andrew B. Freistein

Andrew B. Freistein

Registration No. 52,917

Attorney for Applicants

MRD/ABF/vah
Washington, D.C. 20005-1503
Telephone (202) 721-8200
Facsimile (202) 721-8250
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J. BRANDRUP, E. H. IMMERGUT, and E. A. GRULKE

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**A. ABE
D. R. BLOCH**



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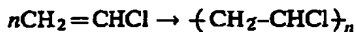
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arrangement, their graphical representation and their names require a special approach.

Often enough, the structure of the polymer has not been sufficiently characterized and the researcher cannot draw its chemical structure. Consequently, no name of the polymer reflecting its structure is possible.

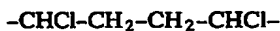
A polymerization reaction for a polymer formed from a monomer such as vinyl chloride can schematically be represented by



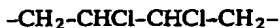
That shows an idealized product. In fact, however, the polymer consists of long-chains of various lengths. The repeating units, $-\text{CH}_2-\text{CHCl}-$, are not necessarily all uniquely oriented and joined in a regular fashion as shown in the idealized structure above. In addition to "head-to-tail" links



other links such as "head-to-head"

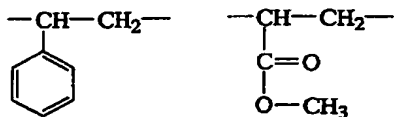


and "tail-to-tail"



can occur, and the exact sequence of all these repeating units usually is not known.

This becomes even more complicated when a copolymer is derived from more than one monomer, such as styrene and methyl acrylate, which contribute two constitutional or monomeric units:



They can combine into a polymeric chain, resulting in many types such as unspecified, statistical, random, alternating, periodic, block, or graft copolymers.

Because the exact structure of the polymer is not always known, two systems of naming polymers exist:

- source-based nomenclature,
- structure-based nomenclature.

1. Source-Based Nomenclature

1.1. Homopolymers Homopolymers are derived from only one species of monomer, which may be the actual starting reactant (or source), or be a hypothetical monomer if the homopolymer is formed by a modification of another homopolymer.

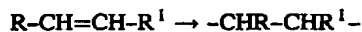
The name of the polymer is formed by attaching the prefix "poly" to the name of the actual or assumed monomer, or the starting reactant (source), from which the polymer is derived.

Examples: poly(acrylic acid)
polyacrylonitrile

polybutadiene
polyethylene
poly(methyl methacrylate)
poly(methyl vinyl ether)
polystyrene
poly(tetrafluoroethylene)
poly(vinyl alcohol)
poly(vinyl acetate)
poly(vinyl chloride)
poly(vinylidene dichloride)

Parentheses are used when the name of the monomer consists of two or more words, and when the monomer has substituents.

These are all olefinic type reactants, from which two carbon atoms originally linked by a double bond form a bivalent group:



where R and R¹ represent a hydrogen atom or a substituent group. Many of these are joined, in turn, to each other but their exact orientation or sequence is seldom known.

On the other hand, different polymers derived from a single monomer and having identical constitutional units can still be differentiated by additional information, such as average molecular weight and other chemical and physical characteristics.

1.2. Copolymers For copolymers, the names of monomers are cited after the prefix "poly". In addition, an italicized connective (infix) is placed between the names of monomers to denote the kind of sequential arrangement by which the constitutional (monomeric) units, derived from each monomer, are related in the structure [4].

Seven types of sequence arrangements are listed with their corresponding connectives:

Type	Connective
unknown or unspecified	-co-
statistical (obeying known statistical laws)	-stat-
random (obeying Bernoullian distribution)	-ran-
alternating (for two monomeric units)	-alt-
periodic (ordered sequence of more than two)	-per-
block (linear arrangement of blocks)	-block-
graft (side blocks chains connected to main chain)	-graft-

Examples: poly[styrene-co-(methyl methacrylate)]
poly(styrene-stat-acrylonitrile-stat-butadiene)
poly[ethylene-ran-(vinyl acetate)]
poly[(ethylene glycol)-alt-(terephthalic acid)]
poly[formaldehyde-per-(ethylene oxide)-per-(ethylene oxide)]
polystyrene-block-polybutadiene
polybutadiene-graft-polystyrene

The names of the monomers are those common or semisystematic names that are encountered most often in the literature of polymer science. The order of citation of monomers in copolymer names is arbitrary.

An equally acceptable alternative scheme for naming copolymers utilizes the prefix "copoly", followed by citation of the names of the monomers, separated by an oblique stroke (a solidus). Parentheses are not needed to enclose monomer names consisting of two or more words.

Examples: copoly(styrene/methyl methacrylate)
stat-copoly(styrene/acrylonitrile/butadiene)
ran-copoly(ethylene/vinyl acetate)
alt-copoly(ethylene glycol/terephthalic acid)
per-copoly(formaldehyde/ethylene oxide/ethylene oxide)
block-copoly(styrene-butadiene)
graft-copoly(butadiene-styrene)

1.3. Nonlinear Macromolecules and Macromolecular Assemblies

Most recently, the source-based nomenclature has been extended for non-linear macromolecules and macromolecular assemblies [5]. The non-linear macromolecules comprise branched, graft, comb, star, cyclic, and network macromolecules. The macromolecular assemblies comprise polymer blends, interpenetrating polymer networks, and polymer-polymer complexes.

The following italicized qualifiers can be used as both prefixes (e.g., *blend*-, *net*-) and infixes (connectives) (e.g., -*blend*-, -*net*-) to designate the skeletal structure of non-linear macromolecules or macromolecular assemblies:

Type	Connective
cyclic	<i>cyclo</i>
branched, unspecified	<i>branch</i>
short-chain-branched	<i>sh-branch</i>
long-chain-branched	<i>l-branch</i>
branched with branch point of functionality <i>f</i>	<i>f-branch</i>
comb	<i>comb</i>
star	<i>star</i>
star with <i>f</i> arms	<i>f-star</i>
network	<i>network</i>
crosslink	<i>ι</i> (Greek iota)
polymer blend	<i>blend</i>
interpenetrating polymer network	<i>ipn</i>
semi-interpenetrating polymer network	<i>sipn</i>
polymer-polymer complex	<i>compl</i>

In naming non-linear homopolymer molecules, the italicized prefix for the skeletal structure of the macromolecule is placed *before* the source-based name of the constituent linear chain.

Assemblies of macromolecules held together by non-covalent bonds are named by a combination of the names of

the constituent macromolecules with an italicized connective between them.

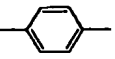
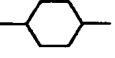

Examples: polystyrene-*comb*-polyacrylonitrile
comb-poly(styrene-*stat*-acrylonitrile)
 polystyrene-*comb*-[polyacrylonitrile;
 poly(methyl methacrylate)]
 4-*star*-polystyrene
star-(polyA-*block*-polyB-*block*-polyC)
star-(polyA; polyB; polyC)
star-(polyacrylonitrile; polystyrene)
 (M_r 100000 : 20000)
net-polystyrene-*ι*-divinylbenzene
net-poly[styrene-*alt*-(maleic anhydride)]-*ι*-(ethylene glycol)
 polystyrene-*blend*-poly(2,6-dimethylphenol)
 poly(methyl methacrylate)-*blend*-poly(*n*-butyl acrylate)
 (*net*-polystyrene)-*sipn*-poly(vinyl chloride)
 [*net*-poly(styrene-*stat*-butadiene)]-*ipn*-[*net*-poly(ethyl acrylate)]

2. Structure-Based Nomenclature

2.1. Regular Single-Strand Organic Polymers For regular organic polymers which have only one species of constitutional repeating unit (CRU) in a single sequential arrangement and consist of single strands only, the name is

poly(constitutional repeating unit),

wherein the repeating group is named as a bivalent organic group according to the IUPAC nomenclature rules for organic compounds [1]. Each such repeating group can consist of simple or substituted subunits such as:

-CH ₂ -	methylene
-CH ₂ CH ₂ -	ethylene
-CH=CH-	vinylene
-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -	hexane-1,6-diyl
-CHCl-CH ₂ -	1-chloroethylene
-COCH ₂ -CH ₂ -	1-oxopropane-1,3-diyl
-COCH ₂ CH ₂ CH ₂ CH ₂ CO-	adipoyl
	1,4-phenylene
	cyclohexane-1,4-diyl
-O-	oxy
-S-	thio
-SO ₂ -	sulfonyl
-NH-	imino
-N(CH ₃)-	methylimino
-NHNH-	hydrazo
	piperidine-1,4-diyl
-SiH ₂ -	silanediyl
-Si(CH ₃) ₂ -	dimethylsilanediyl

Before the total constitutional repeating unit (CRU) can be given a unique name, a single preferred CRU must be selected.

POLYMER CHEMISTRY

Bruno Vollmert

Translated from the German by
Edmund H. Immergut



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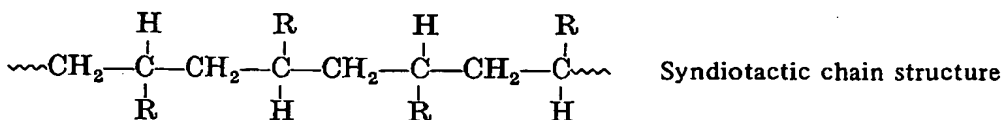
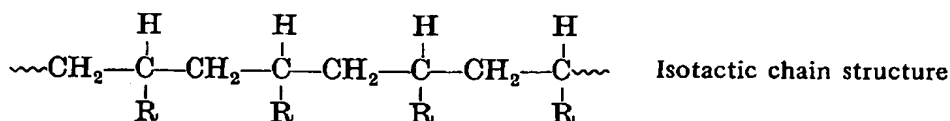
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1,2-addition as well as the formation of *cis*- and *trans*-1,4-polymers. With vinyl compounds one can obtain pure head-to-tail polymerization, but also a mixture of head-to-tail, head-to-head polymerization. (Compare pp. 55-57.)

With vinyl polymers one usually finds 1,3-addition of the substituents. However, it is very difficult to prove that the regularity of the structure is not interrupted every now and then by a different form of addition.

When the carbon atoms in the chain are asymmetric (pseudo-asymmetric) there can be an additional heterogeneity of the chain structure because of the steric position of the substituents along the chain. This has been shown mainly by Natta and co-workers.



The statistically irregular steric structure of most technical polymeric materials is described as *atactic*. The *isotactic* polymers, owing to their regular structure, demonstrate a great tendency to crystallize. When dissolved in "good solvents," however, there are no significant differences between the isotactic and atactic polymers. The best way to represent the isotactic structure is with molecular models (see p. 185-190).

The synthesis of isotactic polymers is usually only possible by means of special stereospecific (stereoregulating) initiators (Ziegler-catalysts). Syndiotactic polymers may also be synthesized through ionic or radical polymerization at low temperatures. In most cases the isotactic and syndiotactic polymers still contain more or less large amounts of atactic structures. Even within a single chain one can have atactic and iso- or syndiotactic segments following one another.

In addition to the irregularity in the chain itself, side chains and chain-branching also strongly influence the properties of the polymers.

12. COPOLYMERS

If only one monomer is involved in the synthesis of a macromolecule, it is called a homopolymer. However, it is equally possible to synthesize macromolecules from two or more different monomers, and these are called copolymers. Table 12 shows a number of macromolecules consisting of two different structural units. These are, however, only of the type in which the different units alternate in a completely regular fashion. In such cases it is possible to combine different structural units into a single repeat unit -AB-. This alternating sequence is, however, only a special case

TABLE 23. Types of Copolymers

1. $\sim A-B-B-A-B-A-A-A-B-A-A-B-A-B-B-B-B-A \sim$
(statistical (or random) sequence)
2. $\sim A-B-A-B-A-B-A-B-A-B-A-B \sim$
or $\sim AB-AB-AB-AB-AB-AB-AB \sim$
(alternating sequence)
3. a) $\sim AB-AB'-AB-AB-AB'-AB-AB-AB'-AB' \sim$
(statistical distribution)
b) $\sim AB-A'B-A'B-AB-A'B-AB-AB-A'B-AB \sim$
(statistical distribution)
c) $\sim AB-A'B-AB'-A'B'-A'B-AB-AB'-A'B'-AB' \sim$
(statistical distribution)
4. $\sim A-C-B-C-A-B-C-C-A-B-B-B-A-A-C-B-C-A \sim$
(statistical distribution)
5. $\sim A-A-A-A \cdots A-A-A-A-B-B-B \cdots B-B-B-A-A-A \sim$
(segment polymers = block-copolymers)

of a series of possibilities as they are shown schematically in Table 23.

Structure 1 shows the most common case of a two-component copolymer in which the two components are distributed randomly along the chain in a certain ratio, which does not always correspond to that of the two monomers in the copolymerizing monomer mixture. This is the chain structure of the majority of the commercially produced copolymers. (For example, those from butadiene and styrene, or butadiene and acrylonitrile, vinylidene chloride and acrylic acid esters, or those from two different acrylic acid esters.) In the same way it is possible to copolymerize three or more monomers together (see structure 4). For example, different acrylic acid esters alone or with styrene, vinyl chloride, acrylonitrile, acrylic acid esters, vinyl pyrrolidone, or also different vinyl ethers by themselves or with isobutylene, acrylic acid esters, or vinyl chloride. Structure 2 corresponds to the normal polyesters and polyamides made from glycols, i.e., diamines, and dicarboxylic acids. There are also combinations of unsaturated compounds, which form copolymers with alternating sequence. To these belong, for example, the following systems: styrene/maleic anhydride, and styrene/acrylonitrile.

Structure 3 allows several possibilities for preparing mixed polyesters or mixed polyamides: (a) for example, from a glycol A and two dicarboxylic acids B and B', (b) from two different glycols A and A' and a dicarboxylic acid B, and (c) from two different glycols A and A' and two dicarboxylic acids B and B'.

There are also many copolymers in nature and, in fact, one can say that it is through copolymerization that nature is able to produce all the many different types of plants and animals. Thus, there is an infinity of different sugars, pentoses and hexoses, and such derivatives as uronic acids and aminosugars from which, by combination in different ways, a large number of polysaccharides are formed. In these different polysaccharides the sequence of the different structural units is by

no means always statistically random. There are some with a certain regular sequence which will then affect the properties of the particular polysaccharide. This is even more characteristic of the proteins, whose chains consist of amino acid residues strung together in a very definite sequence. With certain proteins, for example, insulin or the protein component of tobacco mosaic virus, the sequence of amino acids has now been completely established.

Of some interest is the possibility of combining two different homopolymers into a long chain, as shown in structure 5. Such macromolecules are called segment polymers or block copolymers. They can be prepared in different ways, for example, through the reaction of different polyesters having OH end groups with diisocyanates or through the anionic polymerization of certain monomers with sodium- or lithium alkyls (see pages 164-173).

The common copolymers of unsaturated compounds (structure 1) are of much greater commercial importance. The possibilities of forming copolymers and terpolymers are limited because not every vinyl compound is capable of reacting with every other one to form a copolymer. Styrene, for example, shows very little inclination to react with vinyl chloride or vinyl acetate to form copolymers. In such cases, if one goes to high conversions, the monomers polymerize essentially individually so that a mixture of homopolymers results. As most polymers are not compatible with each other, the mixtures obtained in such cases are not transparent, but opaque white or translucent.

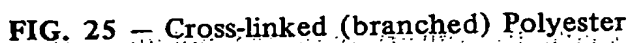
13. BRANCHED AND CROSS-LINKED POLYMERS

In principle, the synthesis of chain-like macromolecules always occurs through the reaction of bifunctional components with each other. This does not mean that the formation of macromolecules requires the monomers to have two preformed functional groups, such as OH groups, COOH groups, NH_2 groups, or $\text{O}=\text{C}=\text{N}$ groups. Often the bifunctional character of the monomers arises only with the addition of an initiator, as for example, with vinyl compounds, which, in the presence of unstable radicals, add to each other as if they were biradicals ("opening of the double bond") or, if ions are added, react like polar compounds.

Another way compounds can attain a bifunctional character through an initiation reaction is the ring-opening of such heterocyclic compounds as cyclic esters (lactones), amides (lactams), and ethers.

The presence of compounds with more than two functional groups leads to the formation of branched and cross-linked macromolecules, as shown in Figures 25 and 26.

Whether a macromolecular compound should be classified as branched or cross-linked is a question of the length (\bar{P}) of the linear chains and of the degree of cross-linking. A branched macromolecule, however, should not be considered equivalent to a partly cross-linked one. As long as the compound is still soluble, it is considered branched, and one speaks of branches or side chains. If, however, the



compound is insoluble (limited swellability) in all solvents, one speaks of cross-linked polymer systems. In the latter case, all chains of the polymer are tied together by covalent bonds, and one can therefore no longer consider the molecules as the smallest part of the material. Figure 28/1 shows in a schematic way the transition from branched macromolecules to a three-dimensional cross-linked material, first through increase in the degree of polymerization of the linear chains and second through the increase in the number of branching and cross-linking points.

There is at a given concentration of cross-linking agent, a critical degree of polymerization at which a branched polymer becomes a completely cross-linked material. The greater the concentration of the cross-linking agent, the lower the critical degree of polymerization. Similarly, for a certain degree of polymerization, one can speak of a critical concentration of cross-linking agent. With solution polymerizations it is particularly easy to observe the attainment and surpassing of the critical degree of polymerization, because often in the space of a few minutes there is a transition from a viscous solution to a more or less solid cross-linked gel.

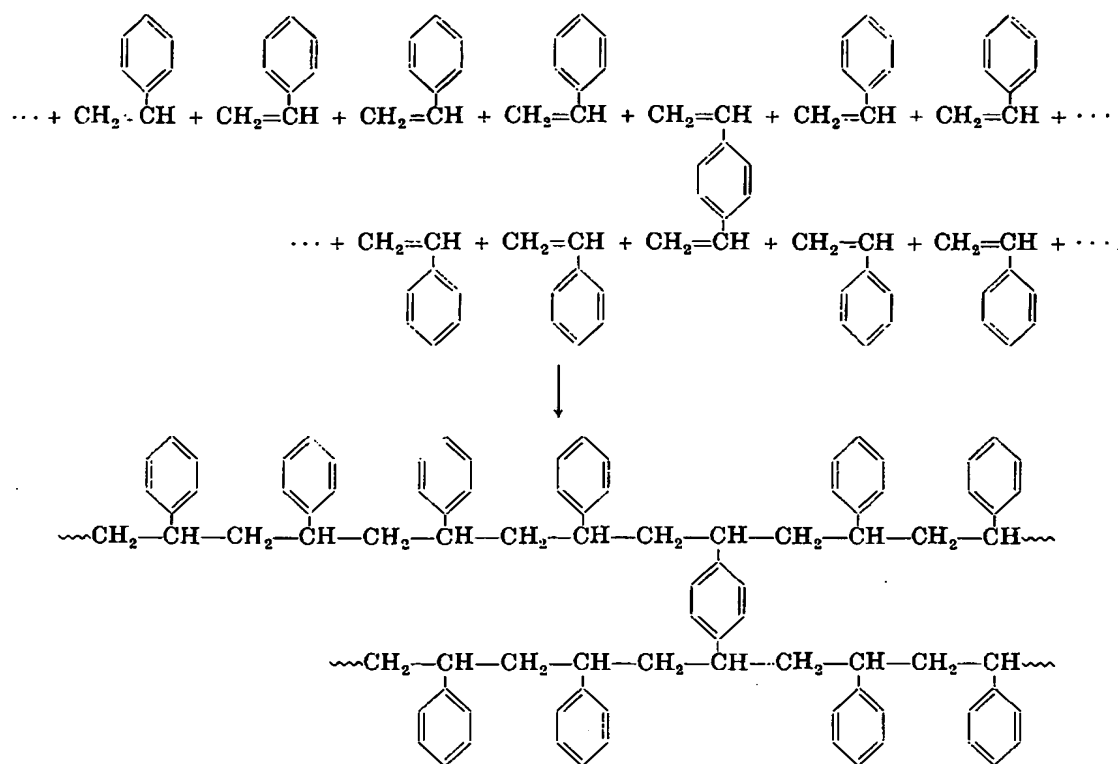


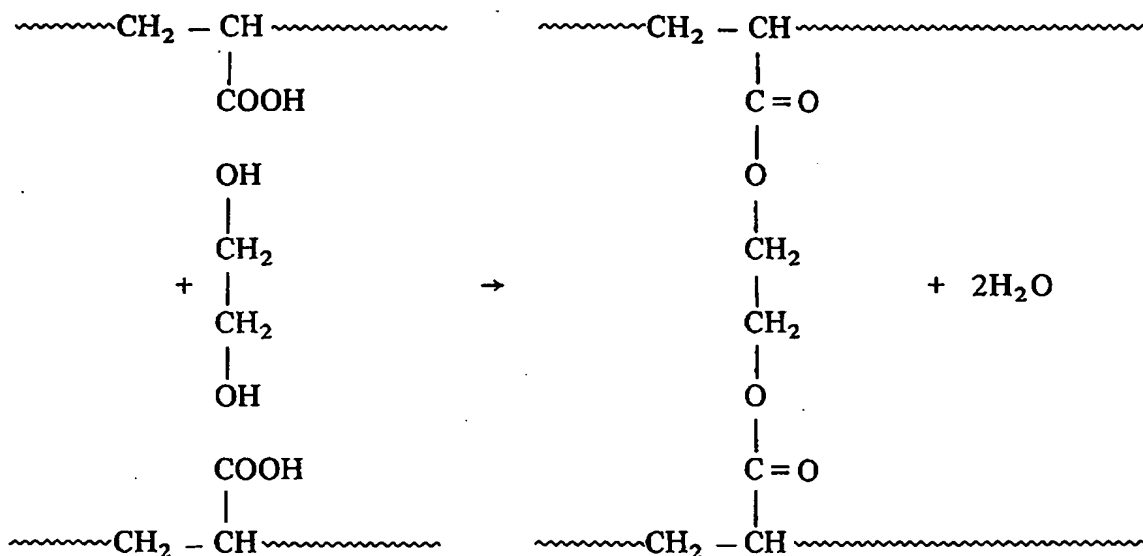
FIG. 26 — Origin of branching (cross-linking) in the polymerization of styrene in the presence of divinylbenzene.

Just as it is possible to convert branched polymers to cross-linked ones by increasing the degree of polymerization, it is possible to convert cross-linked polymers into branched polymers through chain scission. Such a degradation can be brought about in a simple way if one exposes the polymer to strong shearing forces (mechanical degradation). Most macromolecular compounds are thermoplastic, except for some which decompose below their melting point. This means that there is a temperature range in which they show a transition from a hard glassy material into a soft plastic one. This transition usually occurs over a more or less definite stage of rubber elasticity. Thermoplasticity is lost through cross-linking. At low degrees of cross-linking, i.e., large distances between cross-linking points, the cross-linked material remains rubber-elastic above the softening point without being able to flow, whereas strong cross-linking makes the material hard and brittle.

Examples of commercially important cross-linked polymers are vulcanized rubber and the polyester elastomers (for example, Vulcollan). Very tightly cross-linked materials are represented by unsaturated polyester casting resins, ion exchange resins, epoxy resins, and resins based on phenol formaldehyde (Bakelite), melamine-formaldehyde (melamine resins), and phthalic anhydride glycerol (Alkyd Resins). Such resins are infusible, and are therefore called thermosetting resins in contrast to thermoplastic materials.

From a formal point of view one could call all materials with a main valence lattice, such as diamond and quartz, three-dimensional cross-linked macromolecules. Materials with layer lattices, such as mica, talcum, and graphite, could be called two-dimensional cross-linked macromolecular materials.

Cross-linking does not always occur during the polymerization or during the formation of the macromolecular material. It is also possible to first prepare linear polymers with reactive groups or reactive residues, which are then reacted with bifunctional compounds:

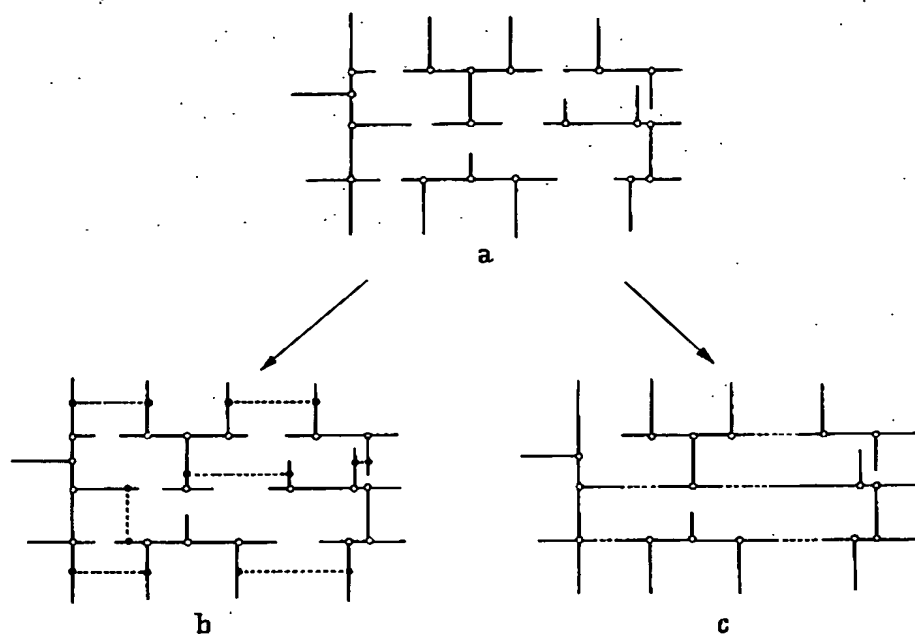


The most important industrial example of this kind of cross-linking is the vulcanization of rubber with sulfur or organic sulfur compounds.

Cross-linked polymers are insoluble in all solvents. However, according to the degree of cross-linking, they can be swollen to a smaller or larger extent. The degree of swelling, that is, the maximum amount of solvent which 1 g of a cross-linked polymer can absorb, can be taken as a measure of the degree of cross-linking (Flory-Rehner-equation). Swollen macromolecules are called gels. Each macromolecular compound exhibits the phenomenon of swelling. The uncross-linked polymers show a gradual transition from swelling to the formation of a viscous solution. However, with cross-linked polymers, swelling is limited (see Chapter 4).

Cross-linking can also come about through secondary valence forces. Examples of macromolecular compounds cross-linked through secondary valence forces are the different polysaccharides and protein gels which play an important role in nature and in living organisms. Depending on temperature and pH, they can occur as solutions or gels. All dissolution of macromolecular compounds occurs through an intermediate stage of the secondary valence gel.

Of particular interest are cross-linked polymers in which the side chains occur at more or less regular intervals along the main chain (Christmas tree structure: Figure 28/2. It is rather difficult to form structures that are completely free of



- a) branched macromolecules
 b) total crosslinking by increasing the number of crosslinking points
 c) total crosslinking by increasing the degree of polymerization of the linear chains

FIG. 28/1 — Molecular branching and crosslinking.

continuous cross-linking (structure a and b). In most cases one obtains systems that correspond to structure c. With all these structures the chains are not really rods, but have a coil structure. This is true not only for the main chains but also for the

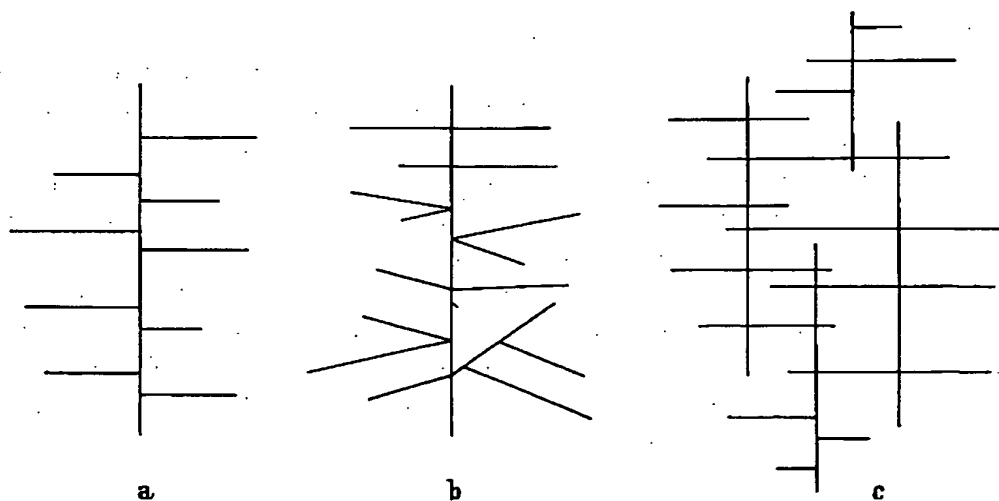
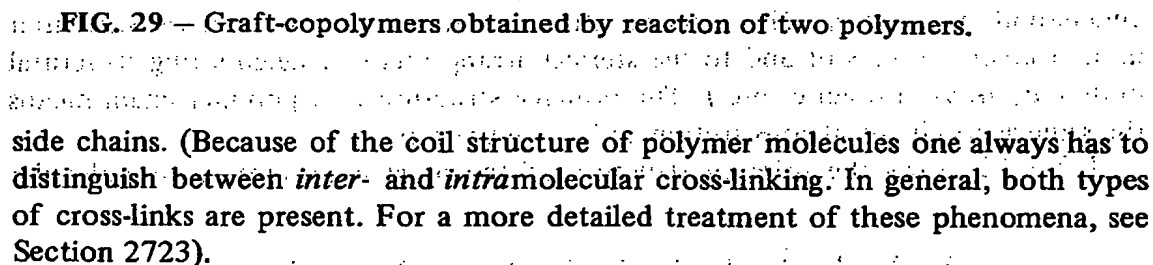


FIG. 28/2 — Branching and crosslinking possibilities



There are essentially two ways of synthesizing graft-copolymers:

- (1) The attachment of side chains which already exist as polymers containing the structural unit B to a polymer with the structural unit A through functional groups X and Y, which must have the property that only X can react with Y, but not X with X and Y with Y (see Figure 29).
- (2) Polymerization of a monomer B on to a polymer $-A-A-A-A-$ with the aid of initiator molecules R_I- which are somehow attached to the main chain or built into it (see Figure 30).

Both block-copolymers and graft-copolymers have properties which are different from those of normal copolymers and from those of the two corresponding homopolymers. Because their preparation is difficult, their industrial importance, especially that of uncross-linked graft-copolymers, is still rather limited. Cross-

linked graft-copolymers, however, (see Figure 28/2, structure c) are prepared in large quantities as polyester casting resins.

PRIMARY, SECONDARY, AND TERTIARY STRUCTURE

A polymer chain consists of a large number of structural units which are to a greater or lesser extent mobile with respect to each other. They can therefore arrange themselves in different ways. All the processes and phenomena which can be observed in the chemistry of low molecular compounds only in a large ensemble of single molecules and which can be described generally with the aid of thermodynamics are found, in macromolecular chemistry, within the region of a single large molecule. Thus one can correctly attribute a state of aggregation to the single macromolecule and, within this meaning, speak of an *intramolecular* or *micro*-Brownian motion. In addition to this motion of single sections or segments of a chain, which may be more or less strong depending on the temperature and the chemical constitution of the chain, the entire macromolecule itself moves (*intermolecular* or *macro*-Brownian motion). The behavior of macromolecular systems is, therefore, especially complicated, not only in respect to thermodynamics (e.g., phase transitions), but also in respect to chemical reactions.

The classification of primary, secondary, and tertiary structure is to be understood as follows. The *primary* structure refers to the kind of structural units a chain consists of and to the sterical arrangement of neighboring structural units (*cis*, *trans*, isotactic, etc.). The primary structure of a polymer chain means the same as its chemical constitution and configuration.

Table 12 shows the primary structure of the most important macromolecular

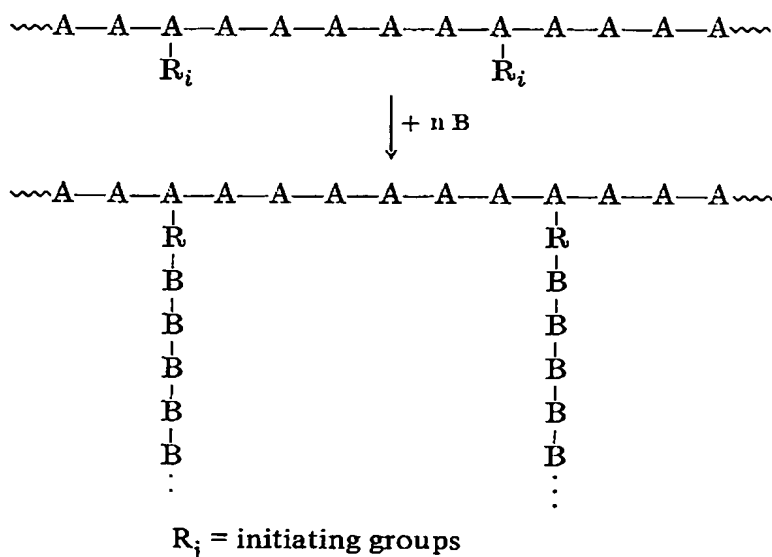


FIG. 30 — Graft-copolymers obtained by polymerizing a monomer in the presence of a polymer.

Secondary structuresExtended chain

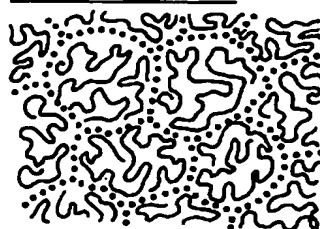
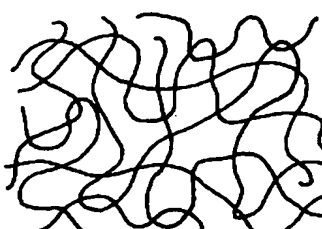
Random coil



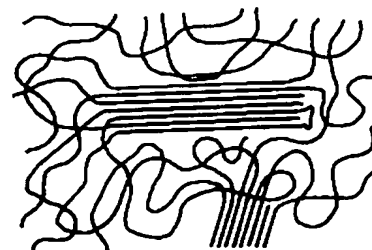
Folded chain



Spiraled chain (helix)

Tertiary structuresCell-structure of
random coils

Spaghetti-structure



Fringed micelle

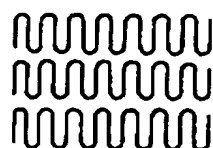
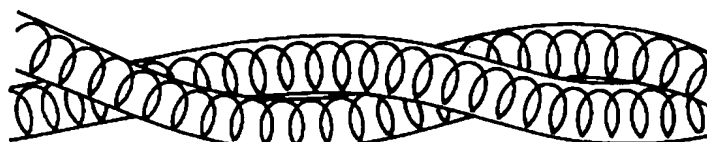
Polymer crystal
with folded chainsOver-spiraling
(super-helix)

FIG. 31 — Schematic representation of secondary and tertiary structures of macromolecules.

compounds. The primary structure affects some characteristics directly—for example, solubility and chemical behavior. It affects most properties, however, only indirectly by influencing the degree of flexibility or mobility of the chain and thus the secondary structure. The secondary structure, in turn, determines and modifies the tertiary structure and thereby the physical behavior of the material.

The *secondary* structure relates to the arrangement of the polymer chain within the range of a single macromolecule, i.e., conformation or the type of aggregation state of an individual macromolecule.

A polymer chain can exist in a number of different shapes: as a completely extended chain, in the form of a random coil, or in the form of a periodically regular arrangement of chain segments (compare Figure 31).

The random coil is, at least with synthetic polymers and with polymer solutions, the predominating type of secondary structure. Its characteristic attribute is the average coil density, which in solution is exactly proportional to the viscosity number and to the molecular weight.

The helix plays a most important role with proteins and nucleic acids. The special stability of these helices, even in aqueous gels and in solutions, is caused by hydrogen bonds between adjacent turns in the helix, or, in the DNA double helix, between certain substituents.

The *tertiary* structure, which is strongly influenced by the secondary structure, is concerned with the arrangement of the macromolecules to form more complex aggregates. As Figure 31i shows, a large variety of tertiary structures is possible. The tertiary structure can extend uniformly throughout the whole polymeric material; however, association of two or more tertiary aggregates can lead to *quaternary* structures, which occur quite often in nature. Hemoglobin, for example, the component of the red blood cells responsible for the transportation of oxygen, consists of particles with four subunits, which are formed in turn by a particular folding of helices.